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NNN APPROACHES TO THE SYNTHESIS OF NOVEL ORGANOSILANES

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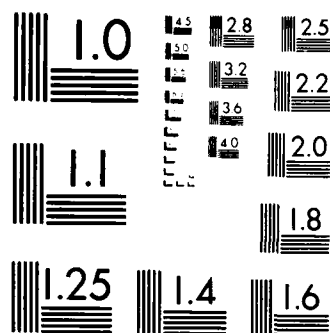
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## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>AD-A190 042</b>			1b. RESTRICTIVE MARKINGS <b>DTIC ELECTE</b>										
3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release Distribution Unlimited			5. MONITORING ORGANIZATION REPORT NUMBER(S) <b>AFOSR-TR. 88-0178</b>										
6a. NAME OF PERFORMING ORGANIZATION North Dakota State Univ.		6b. OFFICE SYMBOL (If applicable) <b>NC</b>		7a. NAME OF MONITORING ORGANIZATION AFOSR/NC									
6c. ADDRESS (City, State, and ZIP Code) Fargo, North Dakota 58105			7b. ADDRESS (City, State, and ZIP Code) Building 410 Bolling AFB 20332										
8a. NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (If applicable) NC		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR 84-0008									
8c. ADDRESS (City, State, and ZIP Code) Building 410 Bolling AFB 20322			10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO. 61102F</td><td>PROJECT NO. 2303</td><td>TASK NO. B2</td><td>WORK UNIT ACCESSION NO.</td></tr></table>		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. B2	WORK UNIT ACCESSION NO.					
PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. B2	WORK UNIT ACCESSION NO.										
11. TITLE (Include Security Classification) New Approaches to the Synthesis of Novel Organosilanes													
12. PERSONAL AUTHOR(S) Philip Boudjouk													
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 11/1/83 TO 10/31/87		14. DATE OF REPORT (Year, Month, Day) 88, 1, 5									
15. PAGE COUNT 21													
16. SUPPLEMENTARY NOTATION													
17. COSATI CODES <table border="1"><tr><td>FIELD</td><td>GROUP</td><td>SUB-GROUP</td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>			FIELD	GROUP	SUB-GROUP							18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Ultrasound, Sonochemistry, Silicon, Organosilanes, Organoselenium, Hydrosilation, Silylenes, Silaceneum	
FIELD	GROUP	SUB-GROUP											
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>The objectives of this program for the period 11/1/84 - 10/31/87 were</p> <ol style="list-style-type: none"><li>1) to continue to extend our research on ultrasonically accelerated reactions;</li><li>2) to continue to develop the new chemistry of low temperature generated silylenes containing large groups on the silicon atom;</li><li>3) to develop routes to silylenium ions in solution and investigate their chemistry;</li><li>4) to develop the chemistry of spiropentasilane derivatives;</li><li>5) to initiate programs in the syntheses of novel silicon-chalcogenide and silicon-transition metal compounds; and,</li><li>6) to investigate the electrochemistry of functionalized organosilanes.</li></ol> <p>In this report we summarize the results obtained in trying to meet these objectives.</p>													
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified										
22a. NAME OF RESPONSIBLE INDIVIDUAL Anthony J. Matuszko			22b. TELEPHONE (Include Area Code) (202) 767-4963										
			22c. OFFICE SYMBOL NC										

AFOSR-TR. 88-0178

"NEW APPROACHES TO THE SYNTHESIS OF NOVEL ORGANOSILANES"  
FINAL TECHNICAL REPORT SUBMITTED TO THE  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
FOR GRANT No. 84-0008  
FOR THE PERIOD NOVEMBER 1, 1983 THROUGH OCTOBER 31, 1987

BY

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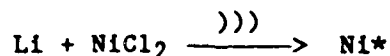


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#### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objectives of this program for the period 11/1/84 - 10/31/87 were 1) to continue to extend our research on ultrasonically accelerated reactions; 2) to continue to develop the new chemistry of low temperature generated silylenes containing large groups on the silicon atom; 3) to develop routes to silylenium ions in solution and investigate their chemistry; 4) to develop the chemistry of spiropentasilane derivatives; 5) to initiate programs in the syntheses of novel silicon-chalcogenide and silicon-transition metal compounds; and, 6) to investigate the electrochemistry of functionalized organosilanes. In this report we summarize the results obtained in trying to meet these objectives.

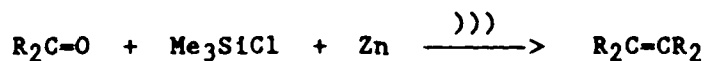
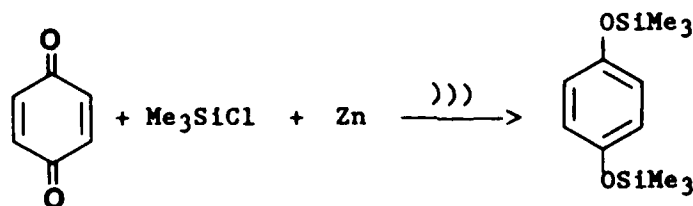
We use ultrasound to prepare the nickel powder from nickel chloride and lithium:



Our examples are the first synthetically successful nickel-catalyzed hydrosilations. The literature on this metal as a catalyst in either heterogeneous or homogeneous form reports very low yields of silicon products. We are investigating the scope of this reaction in detail because of the important economic implications of replacing platinum, which adds more than \$0.12 to cost of each pound of hydrosilated compound, with the much cheaper nickel.

#### Reductive Silylation of Carbonyls

In addition to the hydrosilation reaction described above, we discovered that ultrasound will promote the reductive silylation of carbonyl compounds in the presence of zinc and trimethylchlorosilane and will, in some cases, deoxygenate ketones and aldehydes.

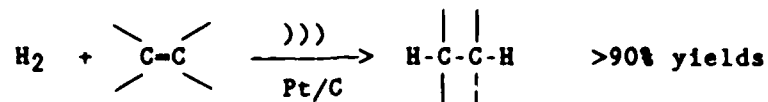


for benzaldehyde and 1-indanone

The latter reaction holds promise as a new olefin synthesis and is especially attractive because the conditions are mild: room temperature, atmospheric pressure and short reaction times (2-5 hrs). Moreover, the reagents are inexpensive and readily available.

### Hydrogenation of Olefins

We have extended our studies of ultrasonically accelerated reactions to three phase systems. Using a high intensity ultrasonic probe fitted with a stainless steel vessel we have been able to hydrogenate olefins at 0°C in less than 2 hours. The hydrogen is under only 2 atmospheres of pressure!

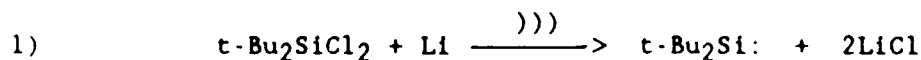


The catalyst is the traditional platinum on carbon with no special preparation and is used in only very small quantities (approximately 0.001 mole percent compared to the quantity of olefin).

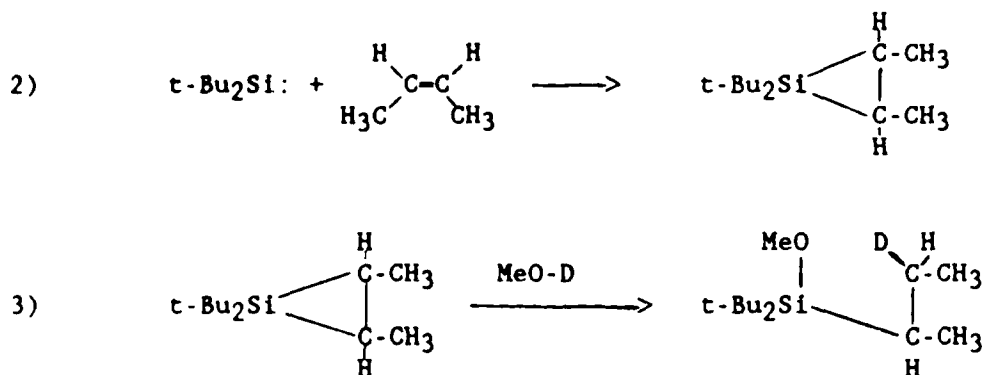
### Chemistry of Low Temperature Generated Silylenes

Several years ago we reported the room temperature synthesis of d-t-butyl-silylene, a highly hindered silylene with the distinct possibility of forming a triplet ground state.<sup>2</sup> The possibility for this unique ground state arises from the large size of the t-butyl group and the potential that the huge steric requirement might force the divalent intermediate into a linear geometry and therefore a triplet state-all silylenes reported to date have been ground state singlets.

Last year we reported in our annual report the completion of the definitive Skell experiment that demonstrates that this new silylene is indeed a singlet and that there is little or no triplet present at ambient conditions. Using the sequence of reactions below we have very convincing evidence:

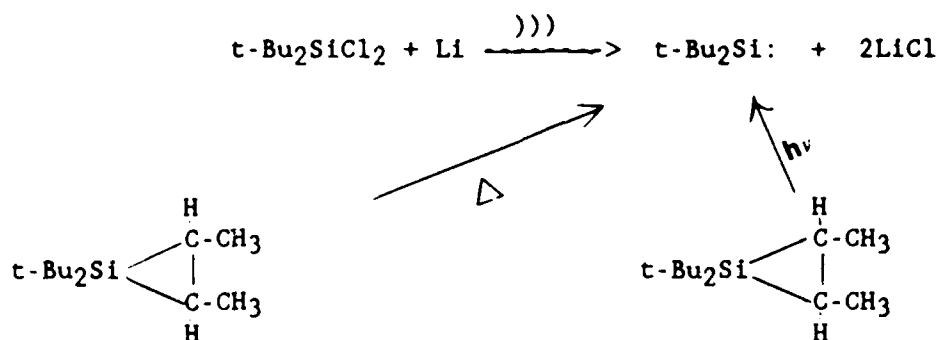






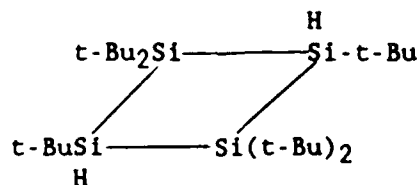
The deuterium-containing carbon in the final product is chiral and its stereochemistry defines the geometry of the silacyclopropane from which it is derived. In summary, the reaction sequence demonstrated that the silacyclopropane was formed by concerted addition to the cis-butene and that there was no stepwise addition to the double bond. Stepwise addition would give some trans dimethyl stereochemistry to the three membered ring and methanolysis would yield a different stereoisomer from the one obtained. Concerted addition is a singlet reaction, stepwise addition is more typical of triplets.

We now wish to report that we have isolated the three membered ring from the reaction of di-*t*-butylsilylene with cis-butene to obtain unequivocal proof that this silylene is a ground state singlet. There is only one product from this reaction, cis-2,3-dimethyl-1,1-di-*t*-butylsilacyclopropane, a very stable compound that exhibits unique reactivity in that, despite the absence of chromophores like phenyl or vinyl groups, has an absorption above 254 nm and can be photolyzed. The consequence: we have shown that this silacyclopropane can now liberate di-*t*-butylsilylene by room temperature photolysis. Alternatively, we can pyrolyze the ring system to give the same species. The net result of all this is that we now have three convenient routes to a reactive intermediate that had been sought after for at least three decades.



These intermediates are very useful for building larger more complex silanes and polysilanes. We have begun investigating the synthetic potential of our method of generating silylenes and we have found that they are indeed very satisfactory as building blocks. Using silylenes generated in this fashion we have been able to prepare novel disilanes and trisilanes as well as some very unusually bulky compounds containing only one silicon atom.

The most significant result of this "building block" is the synthesis of the first stable cyclotetrasilane with functional groups on the silicon atoms:

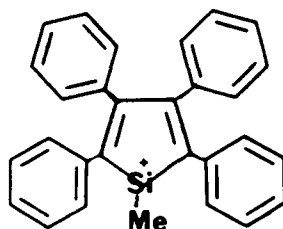


We have prepared this novel compound in yields as high as thirty percent and we have just completed its crystal structure. The unusual aspect of the structure of this compound is that the hydrogen atoms are trans and perpendicular to the nearly planar ring. Most other rings of this size are puckered.

#### Silylenium Ions In Solution

We have undertaken an effort to prepare stable silylenium ions in solution

to pursue the possibility that they may serve as useful molten salts in electrochemical applications or as novel initiators for the polymerization of halocarbons. The system currently under investigation is the silole below:

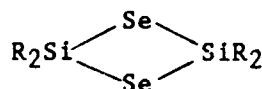
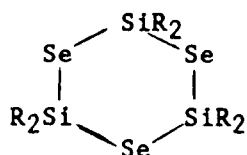


We have completed a series of experiments which indicate that this system may readily produce silylenium ions. For example, hydride abstraction from the silole gives a solution which has a conductance which parallels very closely the conductance of the known organic ionic salt, triphenylcarbenium tetraphenylborate. Stabilization of this silylenium ion is probably from two sources: vinyl stabilization from the two olefinic bonds in the ring system and steric hindrance from the phenyl groups on the ring and on the silicon. We will be examining this system very carefully in the coming year because there are only two examples in the literature of this kind of species.<sup>3</sup> This species has a particularly novel aspect to it: If in fact it is a charge separated silylenium ion then it is the first example of an *antiaromatic* species containing silicon.

#### Silicon-Selenium Heterocycles

The silicon-selenium bond is a reactive polarizable bond that has not been examined closely for its potential in synthesis or in the production of novel materials, in particular, non-linear optic materials. We have prepared the new systems below and completed a preliminary examination of their chemistry. In collaboration with Professor Lyle Parker of this Department we have measured the nonlinear optical activity of this ring system and found that the ring with

R - Ph has frequency doubling (from 1060 nm to 532 nm) with 60% the efficiency of urea. This is a very promising result and provides the basis for further exploration of main group elements as skeletal fragments for nonlinear optic materials.



R = Me, Et, Ph

We can at this stage also report a novel reaction: these ring systems readily fracture to give good yields of new reactive intermediates containing the silicon selenium double bond,  $R_2Si=Se$ . We are examining the chemistry of this species and will be able for the first time make a comparison with related members of the same family, i.e., compare the chemistry and spectroscopic properties of  $R_2Si=C$ ,  $R_2Si=S$  and  $R_2Si=Se$ . Reactive intermediates in which silicon is doubly bonded to another atom have been intensely studied for more than 15 years but only now can a systematic study within a family be executed. We have easy access to all three kinds of species and can compare reaction chemistries. We are collaborating with Hans Bock (Frankfurt) on photoelectron spectroscopic measurements of these reactive intermediates and Dr. Greg Gillispie of our own department to obtain infrared and ultraviolet spectra of these species.

At this point we have demonstrated the existence of this intermediate by trapping reactions with cyclic siloxanes leading to the synthesis of novel ring systems containing silicon, oxygen and selenium.

## Electrochemistry

The electrochemistry of functionalized silanes is poorly developed and, as a result, not well understood. The problems in this potentially important area of chemistry stem from the high sensitivity of halosilanes to water (a persistent contaminant in electrolytes) and the high reduction potentials of these compounds. With considerable effort we were able to obtain the first accurate electrochemical data on a variety of halosilanes (Tables 1 and 2).

Table 1  
Reduction Potentials of Some Mono and Dihalosilanes

$\text{Me}_2\text{HSiCl}$	-3.2v	$\text{Me}_2\text{SiCl}_2$	-3.2
$\text{Me}_3\text{SiCl}$	-3.2	$t\text{-Bu}_2\text{SiCl}_2$	-3.2
$\text{Et}_3\text{SiCl}$	-3.2	$\text{Ph}_2\text{SiCl}_2$	-3.2
$t\text{-BuMe}_2\text{SiCl}$	-3.2	$\text{Me}_2\text{SiCl}_2$	-2.8, -3.0
$\text{Ph}_2\text{HSiCl}$	-3.2	$(t\text{-Bu}_2\text{Si})_2$ Br	-2.9, -3.2
$\text{Ph}_3\text{SiCl}$	-2.85		

Table 2  
Reduction Potentials of Functionalized Silanes

$\text{Me}_3\text{Si-OTs}$	-2.9v
$\text{Me}_3\text{Si-OCPh}_3$	-3.2
$\text{Me}_3\text{Si-OPh}$	-3.2
$\text{Et}_3\text{Si-OAc}$	-3.2
$\text{Ph}_2\text{HSi-OPh}$	-3.2

Moreover, we were able to translate these data to a workable synthetic scheme and produce disilanes in high yields. The approach is quite limited in the laboratory because of the care required for each experiment. There is more cause for optimism on very large scale, however, because the system is amenable to flow synthesis, a scheme that eliminates many of the problems incurred in batch synthesis. Table 3 summarizes some of our results:

Table 3  
Electrosynthesis of Some Disilanes

Me <sub>2</sub> SiHCl	HMe <sub>2</sub> Si-SiMe <sub>2</sub> H	88	82
Me <sub>3</sub> SiCl	Me <sub>3</sub> Si-SiMe <sub>3</sub>	76	60
Et <sub>3</sub> SiCl	Et <sub>3</sub> Si-SiEt <sub>3</sub>	77	67
CH <sub>2</sub> -CHMe <sub>2</sub> SiCl	CH <sub>2</sub> -CHMeSi) <sub>2</sub>	83	73
Ph <sub>2</sub> HSiCl	Ph <sub>2</sub> HSi-SiHPh	90	70

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### Pertinent Recent Research Activities of the Principal Investigator

The research supported by AFOSR through grants 80-0239 and 84-0008 has led to over twenty five papers (including two reviews) and three book chapters. The thrust of our work has been in organosilicon chemistry but, as a result of our efforts to improve the reaction rates of organosilanes, we developed a program to investigate the effects of ultrasonic waves in synthesis. This relatively new area is now known as "sonochemistry" and it is growing rapidly. The AFOSR is well-known as one of the first to support research in this field.

That the interest in sonochemistry is escalating seems clear.

- 1) Symposia: two symposia have already been held that focussed on the chemical effects of ultrasonic waves, the first at the University of Warwick, England, April 1986 as part of the Annual Chemical Congress of the Royal Society of Chemistry. A second was held as part of the ACS Meeting in Anaheim, California, September 1986. The PI was an invited speaker for both symposia.
- 2) Research papers: while it is difficult to arrive at an exact figure for the the number of papers dealing with ultrasonic waves in synthesis, the recent activity in sonochemistry have justified several reviews. Suslick has a major review on mostly homogeneous sonochemistry and the PI has written three on heterogeneous sonochemistry, the most recent has 30 tables and over 250 references dealing mostly with heterogeneous applications. Additionally, numerous reviews have been published in Great Britain, France, Japan and Russia.
- 3) Industrial interest: since our first paper in 1981, industrial interest has been high. Over two-hundred companies have called and written to inquire about sonochemistry and the PI has presented seminars on this topic at about forty

companies in the last four years. Several companies report excellent success on reactions of interest to them but have had difficulty scaling up to more than 25 gallons. Our own work has led to two patents.

Research into the effects of ultrasonic waves required that we investigate many of the traditional organic reactions in addition to those involving silicon. The breadth of our coverage is indicated by the titles of the papers in the Publication List but, in summary, we have demonstrated that nearly every kind of heterogenous reaction can be significantly enhanced when sonicated. By "enhanced" we mean increases in rate or yield and nearly all of the time, both. Reactions involving metals (catalytic and stoichiometric) respond most favorably to ultrasound but solids such as potassium hydride, lithium aluminum hydride, potassium permanganate and aluminum oxide are also activated. Supported catalysts also have greater activity when sonicated.

The nature of cavitation is such that greater reaction rates are possible at lower temperatures. This is mainly the result of reduced vapor pressure in the cavity as it collapses giving rise to a more energetic shock wave. The consequence of this is that we have observed that some reactions progress at low temperatures more efficiently than at higher temperatures. For example, hydrogenation of olefins using hydrogen gas and a commercially available Pt/C catalyst is faster and gives better yields at 0° with ultrasound than at room temperature with vigorous mixing[41]. Several Friedel-Crafts and Diels-Alder reactions respond in the same fashion[52].

The successes in synthesis have begun to attract chemists and physicists to the area that were not formerly involved in ultrasound research. There have been numerous studies on cavitation and related phenomena on very ideal systems, but now that "useful" reactions have benefitted from these phenomena there is a



growing interest to reexamine ultrasound under "real" reaction conditions, i.e., nonaqueous solvents, with organic halides present, with metals under normal reaction conditions rather than highly purified and with conventional ultrasonic equipment. Our plan is get involved in these investigations in a collaborative role until we acquire the expertise to conduct our own studies.

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